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Stephen L. Buchwald, Richard A. Fisher and William M. Davis

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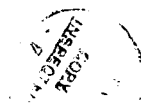
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The Synthesis and Structure of Novel Antimony Thiametallacycles

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ABSTRACT

The first examples of a new class of main group metallacycles, 4, 5-didehydro-2-thiastibolanes, have been synthesized. These compounds were prepared via transmetallation from zirconocene metallacycles. The X-ray crystal structures of the 1-chloro-4,5-dimethyl-4,5-didehydro-2-thiastibolane, **4a**, and the 1-bromo-4,5-diphenyl-4,5-didehydro-2-thiastibolane, **5b**, are reported.

The Synthesis and Structure of Novel Antimony Thiametallacycles

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Recently a dramatic resurgence of interest in the organometallic chemistry of the main group elements has occurred. To a large degree this renewed activity derives from the utility of main group compounds in fields such as ceramics,¹ electronic² and thermochromic materials,^{3,4} and marine antifouling compounds.⁵ The development of general, efficient synthetic methods for the preparation of hitherto inaccessible main group organometallics should greatly enhance progress in many of these fields. In this communication, we report the preparation and characterization of a new class of main group metallacycle, 4, 5-didehydro-2-thiastibolanes, via a transmetallation from zirconium.⁶

We recently reported the synthesis and a study of the reactivity of the thioformaldehyde complex of zirconocene.⁷ In particular, metallacycles **2** can be prepared by treatment of either thioformaldehyde complex **1a** or **1b** with an alkyne. Following the precedent of Fagan and Nugent,⁶ exposure of benzene suspensions of the thiazirconacycles to one equivalent of PhSbCl_2 or SbX_3 ($\text{X} = \text{Cl}, \text{Br}$) results in the rapid and quantitative (by ^1H NMR) formation of the corresponding antimony metallacycles **3-5** and zirconocene dichloride.

Figure 1

With the exception of **3b** the compounds may be isolated in good yield by the removal of benzene *in vacuo*, extraction with hexanes/ether (ca 10:1), and chromatography on alumina III or anhydrous MgSO_4 .⁸ The formation of **3b** can be observed by ^1H NMR⁹ and the compound is indefinitely stable either in solution or as a solid in the presence of Cp_2ZrCl_2 . However all attempts to remove Cp_2ZrCl_2 have either failed or resulted in the decomposition of **3b**. Metallacycles **3a**, **4**, and **5** are all air stable solids and may be stored indefinitely in a dry atmosphere

Compounds **4b** and **5c** were characterized by single crystal X-ray diffraction studies¹⁰ and the ORTEPs are shown in Figures 2 and 3. Compound **4b** is polymeric in the crystalline state. The structure consists of a single stibacycle per asymmetric unit cell. However, the antimony and sulfur atoms of the molecule are mutually bound to the sulfur and antimony atoms of a neighboring molecule (contact distance 3.1\AA) affecting a see-saw geometry about the antimony atoms of the dimeric unit. An additional S-Sb close contact of approximately 3.5\AA gives rise to a puckered net of Sb-S parallelograms in the ac plane of the unit cell (see Figure 2b). The geometry about antimony atom can best be described as a square pyramid with the long contact lying in the basal plane of the unit and the axial position occupied by an intermolecular carbon atom C(3). The sulfur atom of each stibacycle is puckered 0.26\AA out the plane defined by Sb, C(1), C(2), and C(3) in the direction of the second antimony atom to which it is bound.

Figure 2



Figure 2.(a) ORTEP diagram of the dimeric unit of **4b** with selected bond distances (\AA). Selected bond angles ($^\circ$): S-Sb-C(3) = $83.9(4)$, C(1)-S-Sb = $97.1(4)$, S-Sb-Cl = $95.9(1)$, Cl-Sb-C(3) = $95.1(3)$. Intermolecular angles: Cl-Sb-S* = $174.3(1)$, S-Sb-S* = $89.1(1)$. (b) Packing diagram of **4a** showing the propagation of Sb_2S_2 parallelograms through the ac plane of the unit cell, all other atoms omitted for clarity.

The structure of compound **5c** consists of a centrosymmetric dimer. The intermolecular Sb-S distances are in good agreement with those of the dimeric unit of **4b**, however there is no third close contact. As in **4b**, the sulfur atom is perturbed out of the plane (0.24\AA) defined by the other atoms of the metallacycle. The torsional angles defined by the plane of metallacycle and the phenyl substituents at C(1) and C(2) are $103.7(8)^\circ$ and $43(1)^\circ$, respectively. There is also one half molecule of toluene per unit cell. The solvent molecule sits on a C_2 axis and exhibits what appears to be two independent disorders. A meta disorder along the C_2 axis is superimposed on a translational disorder bisected by the axis.¹¹

Figure 3

Figure 3. ORTEP diagram of **5c** with selected bond distances (\AA). Selected bond angles ($^\circ$): Sb-S-C(3) = $95.8(3)$, S-Sb-C(1) = $86.7(2)$, S-Sb-Br = $101.74(6)$, C(1)-Sb-Br = $93.2(2)$. Intermolecular angles: Sb-S-Sb* = $96.75(7)$, S-Sb-S* = $83.25(7)$.

Solution molecular weight determinations indicate that the compounds are monomeric in benzene solution.¹² The ^1H NMR, ^{13}C NMR, and analytical data are all fully consistent with the proposed structures.¹³ The diastereotopic methylene protons of the three 1-phenyl substituted metallacycles, **3a**, **4a**, **5a**, appear as a pair of well resolved doublets in the room temperature ^1H NMR. No significant broadening of the signal occurs on warming to 90°C . In contrast, the diastereotopic methylene protons of the 1-halo substituted metallacycles, **3b,c**, **4b,c**, **5b,c** undergo a concentration dependent exchange reaction. In sufficiently dilute solution ($M \leq 0.015$), the diastereotopic protons of these compounds appear as well resolved doublets at room temperature; the spectra are virtually identical in the methylene region to the spectra of the phenyl substituted

metallacycles. We attribute the fluxional behavior exhibited by the halo-metallacycles to a reversible halide exchange reaction. This conclusion is supported by crossover experiments between 4c and 5b which indicate that a rapid halide exchange is occurring in solution.¹⁴

Investigations of the properties and reactivity of these and related main group metallacycles are in progress.

Acknowledgement. This work was supported by the Office of Naval Research, and in part by Union Carbide, whom we thank. SLB is a Fellow of the Alfred P. Sloan Foundation (1988-90), a Dreyfus Teacher-Scholar (1988-93), an American Cancer Society Junior Faculty Research Awardee (1987-89), an Eli Lilly Grantee (1988-89), and an awardee of the Union Carbide Innovation Recognition Program (1988, 89). We thank the U. S. Department of Energy (Grant No. DE-FG05-86ER-75292) for funding for the Rigaku AFC6R.

Supplementary Material Available: Experimental section containing the preparation and spectroscopic characterization of compounds; crystallographic data and procedures, ORTEP diagrams of 4a and 5c, bond distances and angles, tables of final positional and thermal parameters, and tables of structure factors. Ordering information is given on any current masthead page.

Figure 1

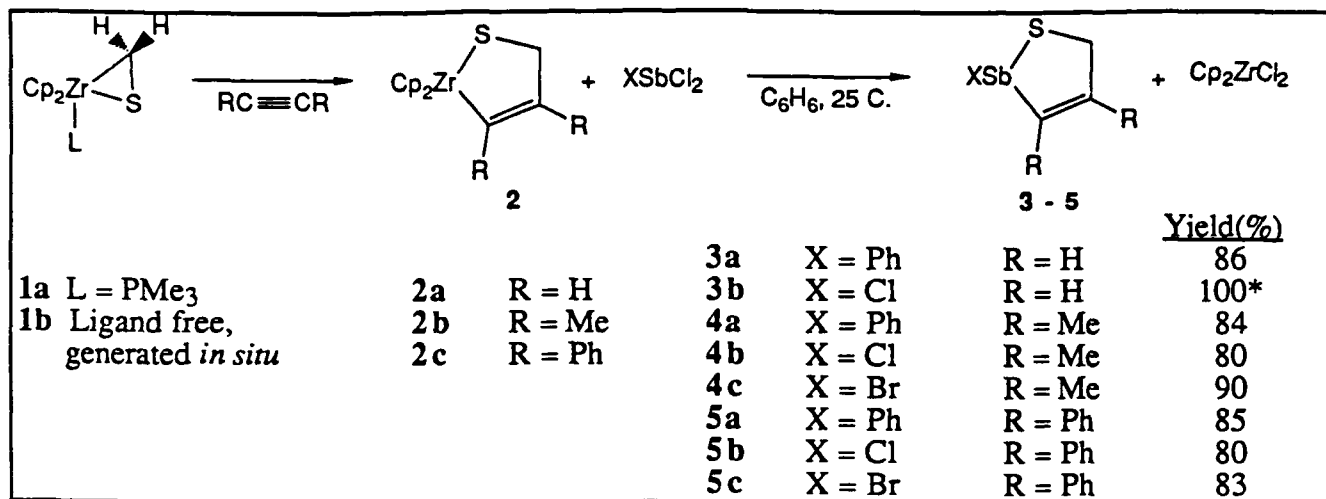


Figure 2a

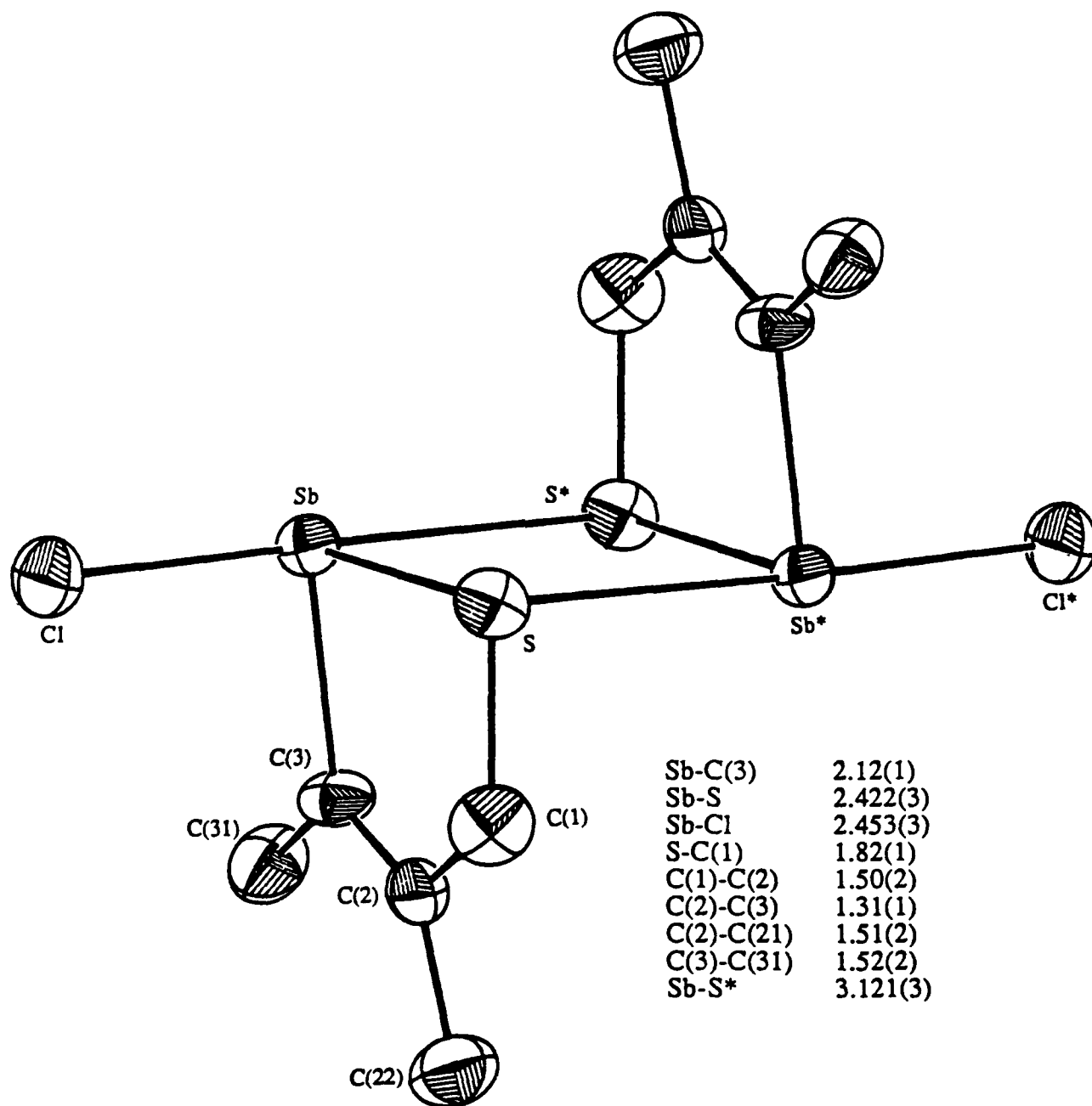


Figure 2b

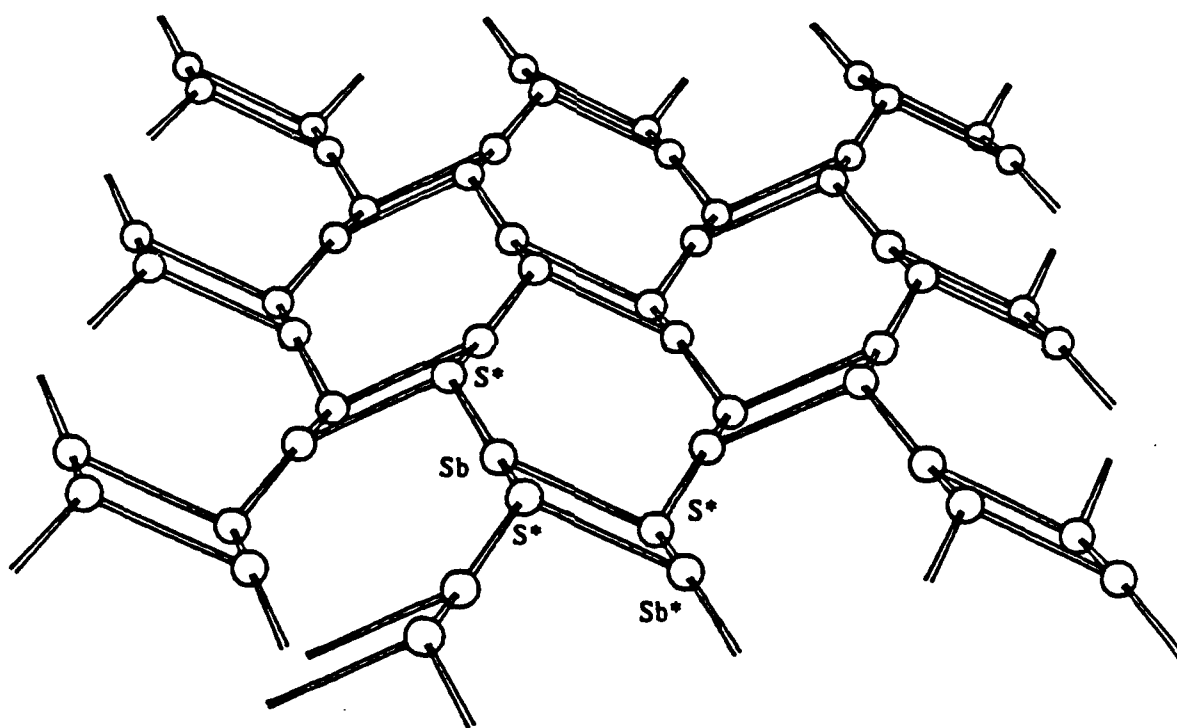
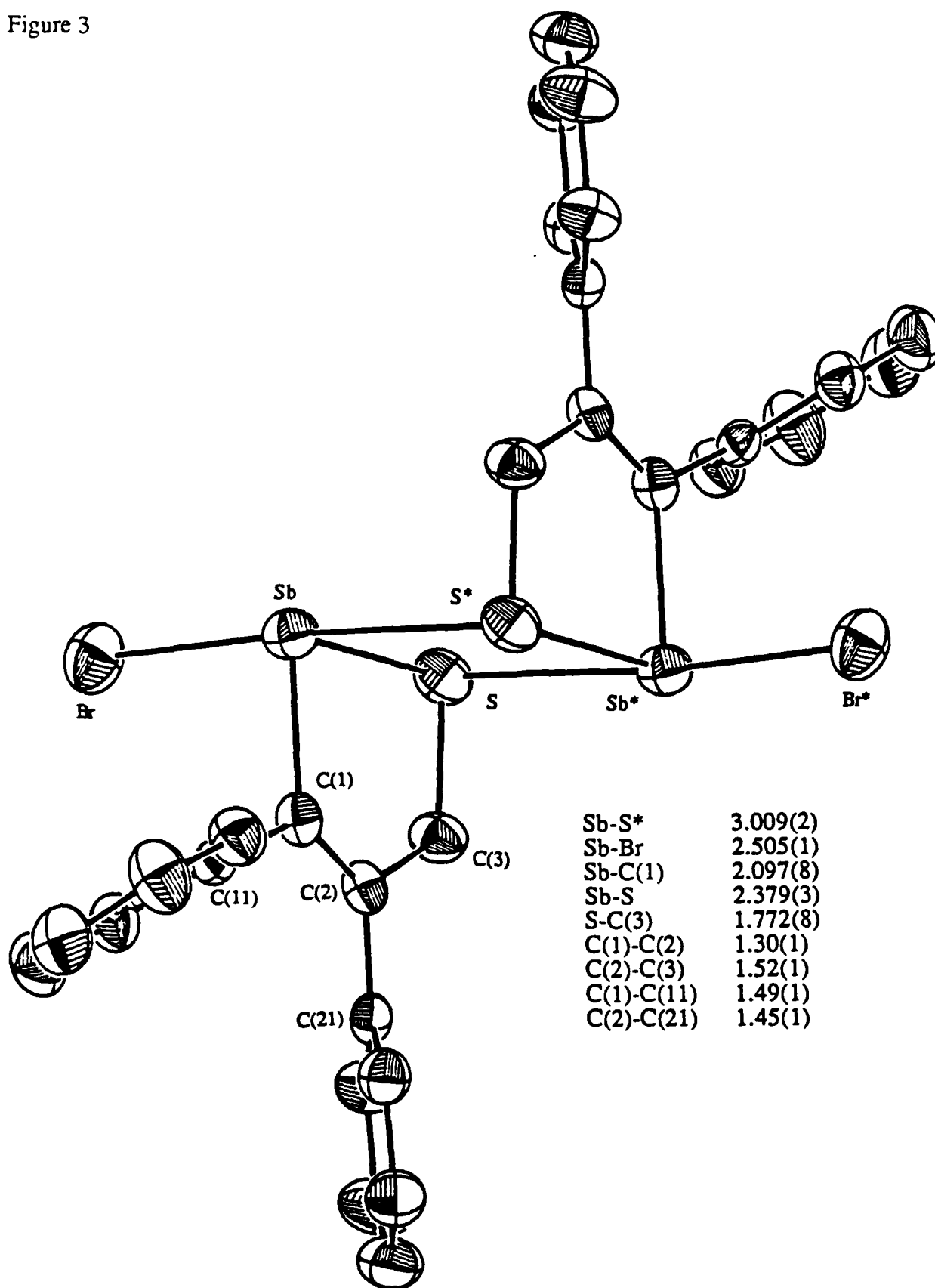


Figure 3



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- ‡ Dedicated to our friend and colleague Professor Dietmar Seyferth on the occasion of his 60th birthday.
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8. Compounds **3a**, **4a** and **5a** were purified by chromatography on alumina III; compounds **4b,c** and **5b,c** were purified by chromatography on anhydrous MgSO_4 .
9. ^1H NMR (300 MHz, C_6D_6) δ 6.98 (dt, $J = 7$ Hz, 1Hz, 1H), 6.74 (dt, $J = 7$ Hz, 1Hz, 1H),
10. Xray data for **4b**: Crystals from toluene- d_8 at room temperature. A colorless prism of **4b** (0.15mm X 0.18mm X 0.18mm) was mounted on a glass fiber. Data were collected at 23° C on a Rigaku AFC6R Diffractometer with graphite monochromated Mo $K\alpha$ radiation, $\lambda = 0.7169\text{\AA}$. Orthorhombic, space group $Pbca$, $a = 11.541(2)\text{\AA}$, $b = 19.104(3)\text{\AA}$, $c = 7.3483(8)\text{\AA}$; $V = 1620.2(8)\text{\AA}^3$; $Z = 8$; $d(\text{calcd}) = 2.11\text{ g/cm}^3$. A total of 1682 reflections were collected (ω - 2θ scan) to 2θ of 50.0°. The structure was solved by direct methods (SHELXS-86). Anisotropic refinement of all non-hydrogen atoms by full matrix least squares (fixed hydrogen parameters, $d_{\text{C-H}} = 0.95\text{\AA}$) resulted in $R = 0.036$ and $R_w = 0.042$.
Xray data for **5c**: Crystals from toluene at -20° C. A colorless block of **5c** (0.65mm X 0.65 mm X 0.65 mm) was mounted on a glass fiber. Data were collected at 23° C on an Enraf-Nonius CAD-4 Diffractometer with graphite monochromated Mo $K\alpha$ radiation, $\lambda = 0.7169\text{\AA}$. Monoclinic, space group $C2/c$, $a = 18.805(2)\text{\AA}$, $b = 7.566(1)\text{\AA}$, $c = 24.416(2)\text{\AA}$; $V = 3358(1)\text{\AA}^3$; $Z = 8$; $d(\text{calcd}) = 1.982\text{ g/cm}^3$. Total of 2575 unique reflections were collected (ω - 2θ scan) to 2θ of 48.8°. The structure was solved by direct methods (SHELXS-86). Non-hydrogen atoms were refined anisotropically with the exception of the solvate presumed to be toluene, *vide infra*. $R = 0.043$, $R_w = 0.051$. The solvate (occupancy = 0.5) was highly disordered about the crystallographic two-fold axis. The model used evenly distributed the toluene molecule about the two fold axis with the symmetry element passing through the ortho- and meta- carbons. Seven peaks from the difference fourier map were assigned a total scattering power equivalent to three carbon atoms. This model precluded the location of the methyl carbons because of the large number of sites over which it is distributed.

- 11 A decay of in the intensity standards was observed with time (18.0%). The decay in intensity was sufficient that only data to 45 degrees in 2θ was used in the structural determination. The presumed culprit for the decay was the gradual loss of solvent from the crystal.
12. a) Compounds **3a**, **4a,b**, and **5c**, were subjected to solution molecular weight determinations as described elsewhere.^{12b} The concentration range for the molecular weight determinations was 0.0560 to 0.1700 M. b) Bercaw, J. E.; Burger, B., J. "Vacuum Line Techniques for Handling Air-Sensitive Organometallic Compounds" In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*. Wayda, A. L.; Darensbourg, M. Y.; Ed.; ACS Symposium Series 357: Washington D. C., 1987; pp 79-102.
13. All new compounds were characterized by ^1H NMR, ^{13}C NMR, IR, combustion analysis and/or high resolution mass spectrometry. Details are available in the supplemental material.
- 14 A full analysis of the fluxional behaviors and reactivity of these compounds will be reported in a full paper.

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